

HYDROGEN BINDING AND DIFFUSION IN DIAMOND*

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INTRODUCTION

The growing interest in the surface and bulk properties of diamond, which are markedly influenced by foreign atoms, is the natural consequence of the evolving technology for low-pressure diamond film and crystal growth.¹⁻⁴ Large hydrogen concentrations are found in natural^{5,6} and man-made diamond, particularly in diamond-like films.⁷ Surface hydrogen is believed to be responsible for low-pressure diamond growth from C₁ and C₂ hydrocarbon fragments, whose identification is under investigation at this time.⁸ During low-pressure growth, hydrogen is essentially a catalyst, maintaining tetrahedral bonding structure at the diamond surface, blocking routes to graphite formation. Bound H atoms are removed by bonding to H atoms from the gas and coming off as H₂. This process momentarily forms active dangling radical orbitals at the surface to which hydrocarbon radicals from the gas bind, in competition with H atoms, ultimately propagating diamond growth. Beyond this, the growth mechanism or mechanisms are not yet understood. We have made model atom superposition and electron delocalization molecular orbital (ASED-MO) studies of the absorption of C₁ and C₂ hydrocarbon species on the diamond (100) and (111) surfaces^{9,10} and have found C₁ species may be able to diffuse on the former surface, but not the latter.

Hydrogen has been rather well studied as an interstitial impurity in silicon, but not in diamond. In silicon it is attracted to substitutional B atoms and poisons their p-dopant properties, affecting the semiconducting properties.¹¹ Recent theoretical works based on quantum mechanical models have shown that an isolated interstitial H atom binds in a Si-Si bond-center site and provides an attractive potential well for second interstitial H to pair with it in an interstitial antibonding site, forming H-Si-H-Si oriented in the [111] direction.¹²⁻¹⁶ For H in diamond, theory has predicted similarly that bond-centered interstitial sites are most stable and a second H is attracted to the antibonding site.¹⁶⁻¹⁹ Infra red (IR) studies of natural diamonds show well-defined stretching and bending excitations at 3107 cm⁻¹ and 1405 cm⁻¹.²⁰⁻²² Recent thermal desorption studies yielded an integrated hydrogen desorption flux of about 10 monolayers of

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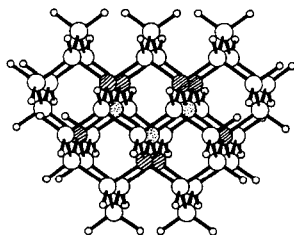
hydrogen between 700 and 1100 K from a polished diamond (1x1) H-covered (100) surface.²³

Standard free energies for alkane formation begin to favor the elements, $C(di)+H_2(g)$, for C_6 and larger, and for all unsaturated hydrocarbon molecules the elements are favored.²⁴ Therefore, it might be expected that sub-surface hydrogen will be released as H_2 . Single bonds between carbon atoms and H_2 single bonds are replacing CH bonds. However, the details of the subsurface H bonding are not known. Interstitial H atoms are likely to be bound weakly as is the case for Si. The release of such H as gas phase H_2 should be very stabilizing and the question of its rate is a kinetic one. If C vacancies exist and H binds to the carbon atoms surrounding these vacancies, and this would be a plausible explanation for the bending and stretching modes seen by IR, then such H would be rather strongly bound. Muon-spin-rotation (μ SR) studies have shown that at temperatures greater than 800 K the +1-charged muon nuclei are in an anisotropic environment,²⁵ which might correspond to such a site. The loss of H, as H_2 following combination with a second vacancy-bound H, would not be stabilizing unless there is massive restructuring which forms C-C bonds and removes the vacancies, since a single H_2 bond would be replacing 2 CH bonds. Whether subsurface vacancies might have several weakly bound H atoms squeezed into them is unknown. Such H might be partially released without the need for restructuring.

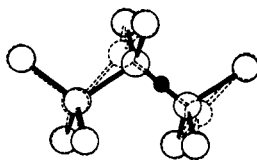
With the above questions in mind, along with what is already known about H in silicon, we have undertaken an ASED-MO study of H atom interstitial and vacancy bonding and diffusion in diamond. We explain our results in terms of the orbital and electronic structures and speculate on the possible effects of p-type dopants. The atomic parameters are those used in the earlier ASED-MO diamond surface work.^{9,10}

INTERSTITIAL H AND ITS MIGRATION

Our C_{46} diamond structure cluster model is terminated by 48 CH bonds to eliminate surface radical orbitals with energies in the band gap, which would interfere with our bulk property calculations. Its structure is shown in 1, with 3 shaded atoms being those relaxed around interstitial H in bond-centered sites, which are calculated to be the most stable interstitial locations, and the hatching identifies the second shell of atoms which were also relaxed in the calculations.

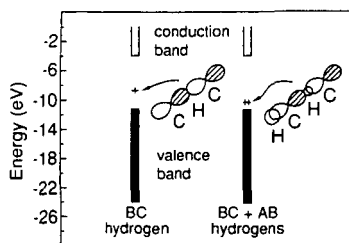


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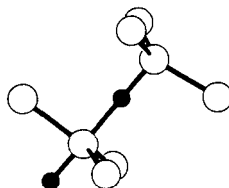


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Rather severe distortions take place to accommodate the bond-centered interstitial H atom, shown black in 2. The interstitial H atom is unstable relative to the free atom by 1.7 eV. The C-C stretching caused by H insertion lowers a localized σ^* orbital from the conduction band into the band-gap as shown in 3, thus stabilizing the radical electron. The band gap orbital has a node at H and the 3-centered C-H-C σ bonding orbital is dispersed in the valence band. It may be expected that a p-type dopant atom, such as B, will stabilize the promoted electron in the band-gap orbital and then interstitial H atoms will be attracted to the vicinity of the dopant atom, as for Si.¹⁵ This will destroy the p-dopant electrical properties of diamond. A second H binds at the antibonding site as shown in 4 1.4 eV more strongly than the first H in the bond-centered site. The second radical electron pairs with the first in



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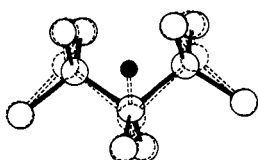


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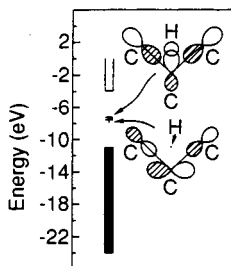
the band-gap orbital, which is stabilized due to overlap between it and the H 1s orbital in the antibonding site as shown in 3. It is expected therefore that p-type dopants will attract a second, and perhaps a third, interstitial H atom.

In the presence of H in the interstitial antibonding site, the bond-centered CH vibrational excitation energy, based on the vibrational force constant in a local-mode approximation, is calculated to be $\sim 1600 \text{ cm}^{-1}$ greater than that calculated in the same way for a CH bond in methane. For the antibonding H it is $\sim 1000 \text{ cm}^{-1}$ greater. Some high-energy vibrational excitations have been observed by IR²² but they match bending overtones and a stretch-bend combination for an isolated, perhaps vacancy, CH bond rather well. Consequently, the concentration of interstitial CH is probably relatively low. An isolated bond-centered interstitial H would, for symmetry reasons, be IR inactive.

An isolated bond-centered interstitial H will migrate to an adjacent bond-centered site by passing through a transition state with the structure shown in 5. The calculated energy barrier is 1.9 eV. Since in the transition state two C-C bonds are stretched, two σ^* orbitals from the conduction band drop into the band gap as shown in 6 and the lower one is C-H non-bonding. This orbital, which takes the promoted electron, is 1.2 eV above the occupied band-gap orbital for the bond-centered site and contributes this much to the H migration barriers. Thus, it is expected that p-dopant atoms will decrease energy barrier for interstitial H atom migration in their vicinity.



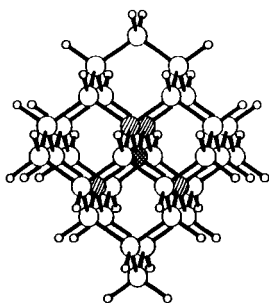
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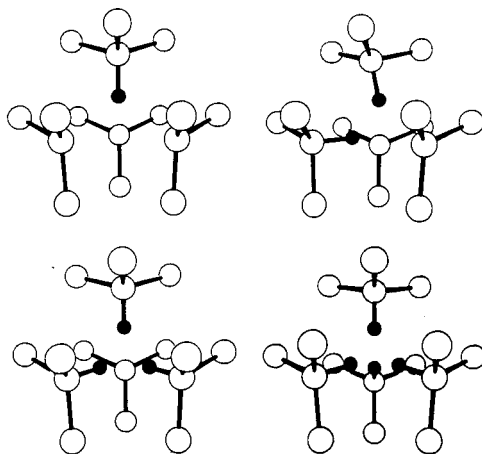
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BINDING OF H ATOMS TO A VACANCY

A vacancy is modeled by removing the cross-hatched atom in 7 and relaxing the hatched atoms. The calculated vacancy formation energy, based on placing the removed C atom on a 3-fold (111) surface site, is calculated to be 6.0 eV. A slight tetragonal distortion, which removes the degeneracy of the doubly occupied t-symmetry set of vacancy radical orbitals, contributes 0.03 eV stability. The structures with 1-4 H atoms in the vacancy are shown in 8. The first H atom forms a CH bond with a strength of 5.3 eV



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8

with respect to its removal from the lattice cluster model. Based on the tertiary C-H bond strength in t-butane, this is a bit over 1 eV too strong. Subsequent H atoms are each calculated to bind about 1 eV more weakly than the previous one. This implies a bulk vacancy could trap up to 4 interstitial H atoms. The H atoms are

crowded quite close together, 1.18 Å when four are present. If there is a substantial number of such H-filled vacancies near the surface, they could contribute to the ~10 monolayers of H₂ desorption observed by Hamza et al.²³ in the temperature-programmed thermal desorption study of the polished (100)-(1x1) surface.

In the local-mode approximation the vibrational excitation of the CH bond for a single H in the vacancy is calculated to be about 3400 cm⁻¹. This is 300 cm⁻¹ higher than the CH stretch observed in natural diamond by IR.²² Since ASED-MO calculations overestimate secondary and tertiary C-H bond strengths, they could well overestimate the CH excitation for H in a vacancy site by ~300 cm⁻¹. Thus our calculations are probably consistent with a CH bond in a vacancy site as the source of the observed 3107 cm⁻¹ stretch. The calculated increases due to adding a second, third, and fourth H to the vacancy are ~400, 700 and 1400 cm⁻¹, respectively. Whether the first two of these are the cause of the observed broad IR absorption around 3700 cm⁻¹ in ref. 22 cannot be established without experimental studies of H concentration dependence and more detailed theoretical analysis.

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